INVESTIGATION OF STERILIZATION OF SECONDARY BATTERIES

SECOND QUARTERLY PROGRESS REPORT

Covering the Period

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ABSTRACT

This report covers the second quarter of an 8 month study to develop a nickel-cadmium cell that, after being thermally sterilized, will yield a power density and cycle life approaching that of a present state of the art nickel-cadmium cell. The evaluation of available separator systems that began in the first quarter is continued. Test results obtained from three different asbestos materials and a high temperature nylon is presented. Data from test cells incorporating two different polypropylenes, a polypropylene-nylon, and an asbestos separator system is given. X-ray diffraction patterns obtained from an unsterilized discharged nickel plate and a sterilized charged nickel plate is also shown.

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I. INTRODUCTION

This report covers the second quarter of an eight month study to develop a nickel-cadmium cell which, after being sterilized according to the Test Approval Procedure, will give a power density and cycle life approaching those of a standard nickel-cadmium cell.

In the first phase of this investigation we evaluated existing separator materials. The procedure was to subject separator test samples to the environment that cells would be required to experience.

In the second phase of this study we incorporated the more promising separator materials in cells. After the cell characteristics had been determined, they were subjected to the Test Approval procedure.

The third phase of this program will go through a more detailed evaluation of the effect of test environment on the individual cell components.

II. FACTUAL DATA

A. SEPARATOR SCREENING TESTS

1. Procedure

In addition to the separator materials listed in the First Quarterly Report, several new materials were received and evaluated. The screening procedure consisted of measuring the length and width of the sample to the nearest 1/64 of an inch. The thickness was measured to the nearest 0.0001 inch, and the weight was determined to the nearest 0.1 mg on an analytical balance.

Each sample under evaluation was then placed in a stainless steel pressure vessel and immersed in 34% potassium hydroxide solution. After sealing, the vessel was placed in an oven which was maintained at 145°C. After a continuous immersion time of 111 hours, the vessel was removed from the oven, the samples were extracted and washed free of electrolyte. After drying the samples, any changes in the length, width, thickness and the weight were noted.

2. Test Results

a. Fuel Cell Asbestos Board (10 mil)

A sample of 10 mil fuel cell asbestos board was received from Johns Manville and subjected to the sterilization routine according to the procedure described above. The sample deteriorated to a pulpy mass, making extraction from the pressure vessel difficult. The color of the material was unchanged and the asbestos fibers appeared to be intact.

b. Fuel Cell Asbestos Board (15 mil)

A sample of 15 mil fuel cell asbestos board was also received from Johns Manville and subjected to the heat sterilization routine as above. The sample deteriorated to a pulpy mass. The extent of the loss of physical integrity was nearly that of the 10 mil board. As with the previous material, the color did not change.

c. High Temperature Nylon

Samples of a high temperature nylon (trade name NOMEX) was received from DuPont. A sample of this material, type 25062, was subjected to the sterilization routine. The material disintegrated completely. No attempt was made to test similar samples with the same base composition.

d. Pure Asbestos

Two asbestos materials were received from the Raybestos Corporation. These materials, designated as 7301 and 7401, are pure asbestos cloths. The type 7401 contains a small percentage of binder. The type 7301 is a pyrolized version of 7401.

Both samples were subjected to the heat sterilization routine. The results, shown in Table I, indicate that the overall shrinkage was slight. The type 7301 asbestos showed smaller dimensional and weight changes than the type 7401.

It was felt that if a second sterilization indicated that the dimensional and weight changes were very slight, the first sterilization could be employed as a pre-treatment. Therefore, a second sterilization was conducted and data, also shown in Table I, indicated that this was the case. It showed that, as in the first sterilization, the type 7301 was less effected than the type 7401.

TABLE I.

EFFECT OF THE TWO STERILIZATION ROUTINES ON THE ASBESTOS SEPARATORS

TYPE 7301				TYPE 7401			
AV. CHANGE IN WIDTH	AV. CHANGE IN LENGTH	AV. CHANGE THICKNESS	AV. CHANGE IN WEIGHT	AV. CHANGE IN WIDTH	AV. CHANGE IN LENGTH	AV. CHANGE THICKNESS	AV. CHANGE IN WEIGHT
1st STERILIZATION				1st STERILIZATION			
+1.3%	-0.3%	-9.2%	-5.1%	+2.0%	-0.8%	-7.9%	-7.3%
2nd STERILIZATION				2nd STERILIZATION			
+0.2%	+0.2%	-1.0%	-1.4%	+1.1%	-0.2%	-5.1%	-2.1%

Limits of accuracy on length ± 0.1%

Limits of accuracy on width ± 0.2%

Limits of accuracy on thickness ± 1%

Limits of accuracy on weight ± 0.01%

The type 7301 asbestos is undergoing further evaluation. A sample was subjected to the heat sterilization procedure. After washing and drying, the separator was incorporated in a five plate cell containing two positive and three negative electrodes. The stack compression was maintained with Lucite pressure jackets. The stack with the pressure jackets was immersed in 34% potassium hydroxide solution. Nine charges and discharges were conducted to determine the capacities and cell voltages. In each operation, the cell was charged at 140 mA until both electrodes were fully charged and then discharged at 0.75 ampere to 1.0 volt. The capacities are given in Table II. No degradation in performance was noted. Scaling the capacity up to the VO-6HS size, the flooded cell would have a capacity of 7.4 Ah. The voltages during discharge were normal, indicating no high electrical resistance in the separator. This separator is now being incorporated into sealed cells for further evaluation.

B. SEALED CELL OPERATION

1. Cells With Asbestos Separators

The First Quarterly Report gave the initial tests of the cells containing type 7410 asbestos. This material contained a high percentage of fiberglass. It indicated that the low capacities and the low pressures on charge lead to the supposition that the quantity of electrolyte was insufficient to maintain acceptable performance. The quantity of electrolyte was raised to 15.0 cc in each cell, and then they were charged at the C/10 rate. On discharge at C/2, 3.0 amperes, all cells, including the controls, gave lower capacity.

TABLE II.

CAPACITIES OF FLOODED CELLS WITH
TYPE 7301 ASBESTOS SEPARATOR

CYCLE	CAPACITY TO 1.0 VOLT *
1	1.57
2	1.64
3	1.74
4	1.64
5	1.65
6	---
7	1.68
8	1.65 **
9	1.58

* Discharge Rate 0.75 A, Charge Rate 140 mA

** Estimated VO-6HS Capacity 7.4 Ah

The cells mentioned above were not equalized prior to charge. In order to determine if this factor caused the reduction in performance, a one ohm resistor was placed across each cell overnight. The cells were then charged again at C/10 for 16 hours and discharged at the C/2 rate. The capacity of the control cells increased 20% while the capacity of the cells with the asbestos separator decreased by approximately 50%.

In order to determine the cause for the low capacity, the can of the cell was employed as an indicating electrode during the discharge. The negative electrode was limiting the capacity. The cells with the asbestos separator were given a saturation charge to determine if the capacity could be reclaimed. On discharge, the capacity was again lower. All further testing was discontinued.

2. Cells With Polypropylene and Polypropylene-Nylon Separators

The First Quarterly Report covered the initial manual charging and discharging of the cells with the polypropylene and polypropylene-nylon separators. The quantity of electrolyte necessary for satisfactory operation has been determined. Several cycles were conducted to stabilize the capacity. Each cycle consisted of charging at the C/10 rate for 19.5 hours and discharging at the C/2 rate. The average capacities are given in Table III.

After discharging overnight with resistors, the cells were placed in the oven with the resistors removed. The oven temperature was maintained at 145°C, and the total immersion time was 37 hours.

In addition to the above cells, a "standard" was also inserted in the oven. This consisted of a welded cover and case to which a pressure gauge was attached. No components were inside the cell,

TABLE III.

CAPACITIES OF CELLS PRIOR TO INSERTION IN THE OVEN

CELL GROUP	SEPARATOR SYSTEM	NO. OF CELLS PER GROUP	CAPACITY TO 1.0V*
1	SM91 Polypropylene	4	6.65
2	EM476 Polypropylene	5	6.55
3	EM124.3 Polypropylene-nylon	5	6.76
4	Pellon Standard Separator System **	2	7.26

* Discharge rate 3.0 Amp.

** Not Placed In Oven

but 15.0 cc of 34% potassium hydroxide was added. The purpose of this device was to observe the pressure in the cell due to the vapor pressure of the electrolyte.

A total of three sterilization routines were conducted. Five cells were fabricated with each separator tested, three for sterilization and two as controls. Prior to, and after each sterilization, all five cells were charged and discharged in series. The effect of the sterilization routines on the cells was assumed to be the difference between the control cells and those that were in the oven. Table IV shows the capacities of the cells with the various separators compared to the control cells with the same separator systems.

In addition to the drop in capacity, the plateau voltages decreased after the sterilization routines. This indicates that the internal resistance of the cells has increased. The drop in the plateau voltages of the cells that were sterilized compared to those of the controls, also is shown in Table IV.

In an attempt to determine whether cells can be sterilized in the fully charged state by maintaining a trickle charge while they are in the oven, fully charged cells were placed in the oven and trickle charged at 100 mA initially. The charging rate was gradually increased to 250 mA and maintained at this rate for 30 hours of the 37 hour sterilization period. During this period, the pressures and voltages were low, as indicated in Table V. The cells were removed and allowed to cool overnight. The following discharge at the C/2 rate, 3.0 amperes, yielded very little capacity.

From the data in Table V, it is evident that the cells in the oven were not on overcharge. This suggests that the self-discharge rate at 145°C is greater than 250 mA.

TABLE IV.

COMPARISON IN CAPACITY BETWEEN CONTROL CELLS
AND THOSE CELLS THAT HAVE UNDERGONE THE STERILIZATION PROCEDURES

SEPARATOR SYSTEM	PERCENT CHANGE COMPARED TO CONTROL CELLS					
	Prior To Steril.	After 1st Steril.	After 2nd Steril.	After 3rd Steril.	Voltage Diff.	Actual* Cap.
Polypropylene-nylon EM 124.3	0%	+ 4.5%	- 2.8%	- 14.6%	-40 mA	5.85 Ah
Polypropylene EM476	+ 2.3%	+ 5.2%	- 0.8%	- 0.8%	-40 mA	5.16 Ah
Polypropylene SM91	+ 7.0%	+ 7.9%	+ 0.6%	+ 0.6%	-60 mA	5.80 Ah

Cells Charged at 600 mA for 16 Hours
Cells Discharged at 3.0 Amperes
* Cells That Were Subjected to the Sterilization Routine

TABLE V.

CELL PRESSURES DURING STERILIZATION OF CHARGED CELLS
AND CAPACITY AFTER STERILIZATION

SEPARATOR SYSTEM	NO. OF CELLS PER GROUP	AVERAGE PRESSURE*	AVG. CAP. OF CELLS	AVG. CELL VOLTAGE	VOLTAGE SPREAD
Polypropylene-nylon EM 124.3	1	54	4.95	1.14	---
Polypropylene EM476	3	53	4.13	1.19	1.14-1.24V
Polypropylene SM91	3	54	4.80	1.22	1.19-1.24V
Control	1	41	---	---	

* At end of 37 hour period. Charging rate 250 mA for last 30 hours.

In order to determine if the capacity was irreversibly lost, the cells were charged at C/10 for 16 hours. After 2 hours of charge, one cell containing the polypropylene-nylon separator developed an electrical short and was removed from the circuit. At the end of charge, the voltages were very high. The average voltages and the spread are shown in Table VI. The subsequent discharge gave lower capacities than experienced after the third sterilization and are shown in the second column. Cell voltages were also higher. After the discharge, the cells were shorted overnight and a short test was conducted. This consisted of charging at C/10 for 10 minutes and monitoring the voltage after a 24 hour stand. All cells showed a minimum 1.18 volts indicating that no electrical leakage had developed.

At the end of this two day stand, high residual pressures were still evident. The cell atmosphere was evacuated and the cells pressurized to 50 psi with oxygen. On the subsequent charge and discharge, the capacities did increase as shown in Column 3. On the third charge, the cell voltages decreased slightly. The discharge at C/2 showed that the capacities were in excess of those at the end of the third sterilization routine.

The foregoing results suggest that sterilization in the fully or partly charged state cannot be accomplished because a degradation in capacity occurs. However, while the degradation in capacity is not completely irreversible, some hydrogen pressure is built up in the cell when the cell is charged-discharged to reclaim the capacity.

While charging and discharging similarly treated cells to determine if the capacity lost during sterilization can be reclaimed, reference electrode measurements were made to determine which electrode was responsible for the loss in capacity. These measurements indicated

TABLE VI.

ELECTRICAL OPERATION OF CELLS AFTER STERILIZATION
WITH TRICKLE CHARGING

	1st CHG. & DISCHG.			2nd CHG. & DISCHG.	3rd CHG. & DISCHG.		
SEPARATOR SYSTEM	AVG. CHARGE VOLTAGE	VOLTAGE SPREAD	AVERAGE CAPACITY	AVERAGE CAPACITY	AVG. CHG. VOLTAGE	VOLTAGE SPREAD	AVERAGE CAPACITY
Polypropylene-nylon EM124.3	1.66	---*	4.95	5.65	1.58	---*	6.20 Ah
Polypropylene EM476	1.67	1.61-1.71	4.13	4.98	1.60	1.60-1.60	5.73
Polypropylene SM91	1.66	1.65-1.66	4.80	5.57	1.60	1.60-1.60	6.22

Charge Rate 600 mA

Discharge Rate 3.0 Amperes

* One Cell in Group

that the loss was due to a degradation at the positive electrode. X-ray examination of the plates before and after sterilization indicated that a recrystallization of active material occurs at the surface of the plates when they are exposed to the high temperature environment in a charged state. This is shown in Figures 1 and 2 (before and after sterilization, respectively) where the $Ni(OH)_2$ peaks relative to the nickel peaks are much more prominent after sterilization.

C. STERILIZATION OF COMPONENTS

Positive and negative stacks were subjected to the Test Approval Procedure. These stacks will be incorporated into cells as specified by Task II of the Work Statement to determine the effect of sterilization in the individual cell components.

III. PLANS FOR FUTURE WORK

1. Asbestos separator Type 7301 will be incorporated in cells. These cells will be operated electrically to determine if this material is suitable as a separator material. The cells will then be subjected to the heat sterilization routine in the discharged state.

2. The cells with the polypropylene and polypropylene-nylon separators will be opened, flooded, and a reference electrode will be incorporated. The cells will be charged and the responsibility of each electrode for the high charge voltages will be determined.

3. The packs that were sterilized will be incorporated into cells according to Task 2 of the Work Statement.

X-RAY DIFFRACTION PATTERN of POSITIVE ELECTRODE AFTER STERILIZATION

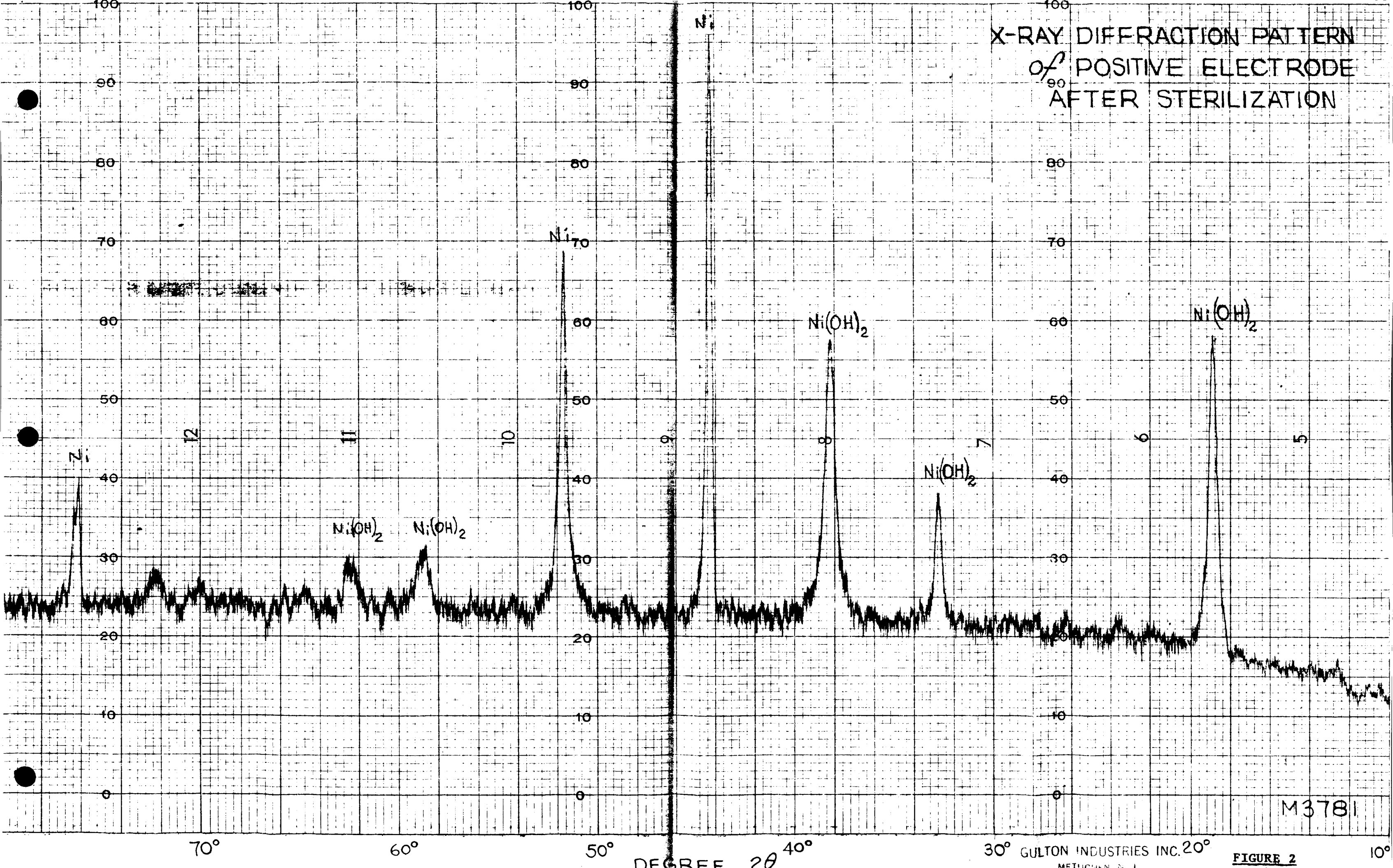

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FIGURE 2

X-RAY DIFFRACTION PATTERN of POSITIVE ELECTRODE BEFORE STERILIZATION

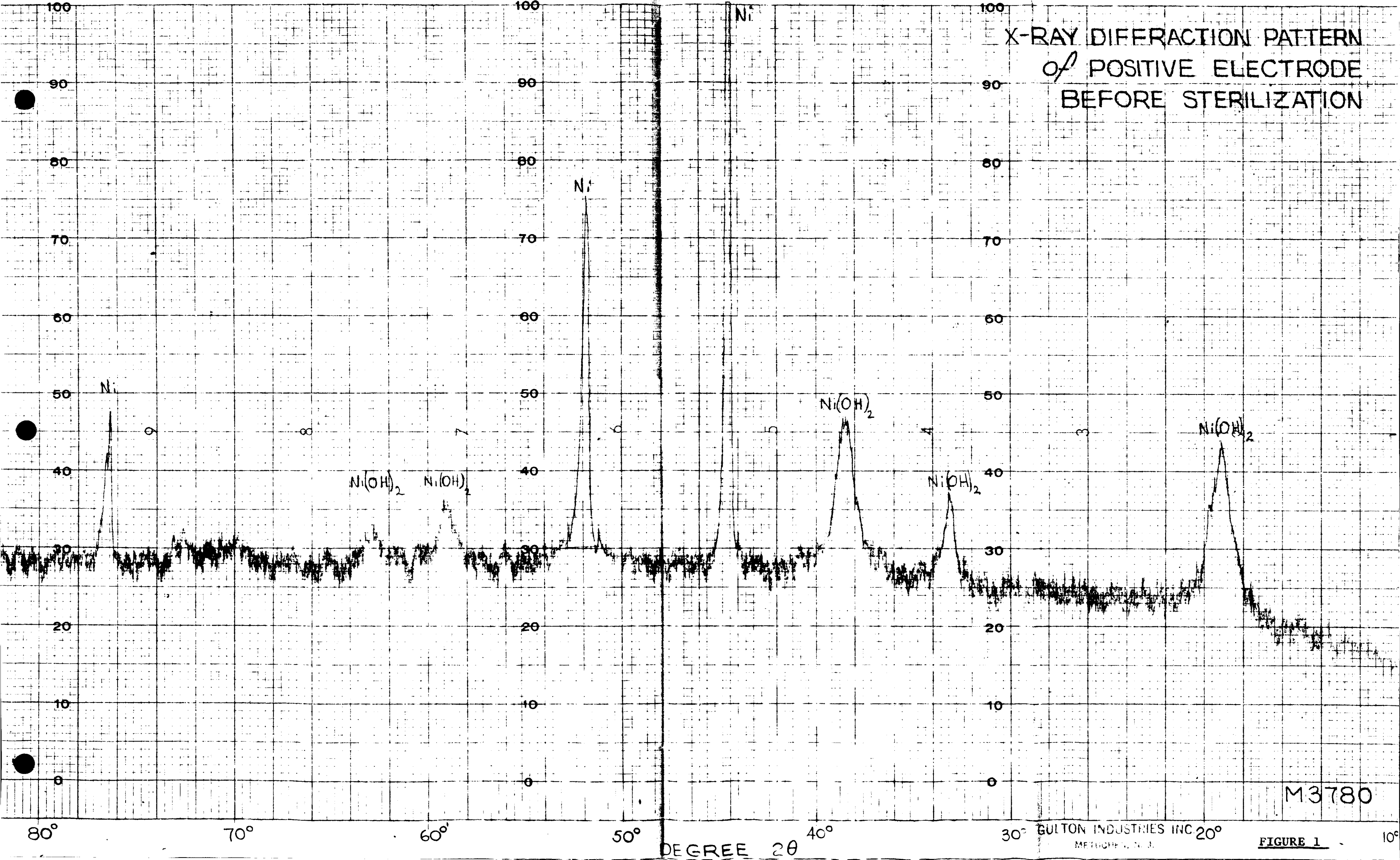

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FIGURE 1